

PAT-NO: JP408100328A

DOCUMENT-IDENTIFIER: JP 08100328 A

TITLE: PRODUCTION OF CARBON FIBER BY VAPOR PHASE
GROWTH

PUBN-DATE: April 16, 1996

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APPL-NO: JP06259030

APPL-DATE: September 29, 1994

INT-CL (IPC): D01F009/127, C01B031/02

ABSTRACT:

PURPOSE: To obtain the subject carbon fiber without necessitating a high-temperature process and particular safety measures by thermally decomposing a hydrocarbon gas with a substrate having catalyst particles dispersed on a heat-resistant substrate.

CONSTITUTION: A substrate holding catalyst particles such as fine particles of metallic Pd dispersed on a heat-resistant substrate is exposed to a hydrocarbon gas (preferably C₂H₄) diluted with an inert gas and heat-treated to effect the thermal decomposition of the hydrocarbon gas and

the vapor-phase growth of carbon fiber. An electronic element, etc., holding the vapor-phase grown carbon fiber as quantum fine line can be produced by forming a proper pattern of the catalyst particles by screen printing, etc.

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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-100328

(43) 公開日 平成8年(1996)4月16日

(51) Int.Cl. ⁸	識別記号	序内整理番号	F I	技術表示箇所
D 0 1 F 9/127				
C 0 1 B 31/02	1 0 1	Z		

審査請求 未請求 請求項の数9 F D (全 5 頁)

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(54) 【発明の名称】 気相成長炭素繊維の製造方法

(57) 【要約】

【目的】 工業的生産に適用可能で、高温のプロセスや、特別な安全対策など困難なプロセスを必要としない気相成長炭素繊維の製造方法を提供する。

【構成】 耐熱性の基体上に金属Pd微粒子を分散してなる基板を不活性ガスで希釈した炭化水素ガスに曝露して熱処理し、炭化水素ガスの熱分解を行う工程を有する気相成長炭素繊維の製造方法。炭化水素ガスはC₂H₄が好ましい。

【特許請求の範囲】

【請求項1】 耐熱性の基体上に触媒微粒子を分散してなる基板を不活性ガスで希釈した炭化水素ガスに曝露して熱処理し、炭化水素ガスの熱分解を行う工程を有することを特徴とする気相成長炭素繊維の製造方法。

【請求項2】 前記触媒微粒子が金属Pdである請求項1記載の気相成長炭素繊維の製造方法。

【請求項3】 前記気相成長炭素繊維の製造方法において、上記金属Pd微粒子の形成方法が、絶縁性基体に有機Pd錯体溶液を塗布する工程と、該有機Pd錯体溶液を塗布した基体を大気中または酸化雰囲気中で熱処理しPdOとする工程と、該PdOを不活性ガスで希釈した還元性ガス中で熱処理して金属Pdとする工程を有する請求項2記載の気相成長炭素繊維の製造方法。

【請求項4】 前記PdOを不活性ガスで希釈した還元性ガスで熱処理する工程において、該還元性ガスがH₂ガスである請求項3記載の気相成長炭素繊維の製造方法。

【請求項5】 前記PdOを不活性ガスで希釈したH₂ガスで熱処理する工程において、H₂の濃度が4vol%未満である請求項4記載の気相成長炭素繊維の製造方法。

【請求項6】 前記請求項3記載の不活性ガスで希釈した還元性ガスで熱処理する工程において、該還元性ガスが請求項1記載の炭化水素ガスと同一である請求項1乃至3のいずれかの項に記載の気相成長炭素繊維の製造方法。

【請求項7】 前記請求項1または6に記載の不活性ガスで希釈した炭化水素ガスを用いる還元及び熱分解の工程において、該炭化水素ガスがC₂H₄である請求項1または6記載の気相成長炭素繊維の製造方法。

【請求項8】 前記不活性ガスで希釈したC₂H₄の濃度が2.7vol%未満である請求項7記載の気相成長炭素繊維の製造方法。

【請求項9】 前記炭化水素ガスの熱分解工程の熱処理温度が450℃以上である請求項1記載の気相成長炭素繊維の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、気相成長炭素繊維の製造方法、特に生産技術上、より容易な工程を用い、かつ大量生産可能な気相成長炭素繊維の製造方法を提供するものである。

【0002】

【従来の技術】従来、炭素原子60個から構成され、サッカーボール状の構造をもつC₆₀の大量合成法が報告(Kratschmer, et. al.: Nature 347 (1990) 354)されて以来、炭素のクラスターであるフラーレンの一族や、これを一方向に引き伸ばした構造を持つカーボンナノチューブの様々な性質

に興味をもたれ、数多くの研究が行われている。

【0003】とりわけ、アルカリ金属原子をドープしたC₆₀の結晶が高い臨界温度をもつ超伝導性を示すことは注目を集めた。このほかにも、これら炭素クラスターは新規な電子素子や、固体潤滑材などとしての応用が期待されており、様々な観点からの応用を目指して、旺盛な研究が進められている。

【0004】気相成長炭素繊維は、カーボンナノチューブよりやや大きなクラスターであるが、炭化水素樹脂繊維を高温で炭化した炭素繊維と比較して、良好な結晶性をもち、特徴ある用途が期待されている。

【0005】現在、この気相成長炭素繊維を製造する代表的な方法はベンゼンの熱分解による気相成長法である。この方法は、酸化鉄などの鉄化合物を基板とし、950～1000℃程度で、高純度の水素をキャリアガスとしたベンゼンの蒸気に接触させる。まず、基板の一部が還元されFe微粒子を形成する。この微粒子表面の触媒能により、表面に炭素が析出しはじめる。この炭素がFe微粒子の後方に繊維状に成長し、微粒子を持ち上げながら成長を続ける。

【0006】この方法では、Fe微粒子の存在が不可欠であり、また金属Fe微粒子を基板に噴霧したものを用いる方法も行われている。(稲垣道夫:「炭素材料工学」72頁、日刊工業新聞社発行 1985年)

【0007】

【発明が解決しようとする課題】上記の方法は、工業的に利用可能ではあるが、いくつかの問題点がある。第1に、工程中に、1000℃程度の高温のプロセスが必要であり、装置が大掛かりになり、電力の消費が大きいなどコスト上昇を招く恐れがある。第2に、高純度の水素を用いるため、爆発事故防止の対策が必要となる。とりわけ上記の高温のプロセスに用いることから、特に厳重な対策が求められ、これもコスト上昇の要因となる恐れがある。

【0008】また、基板にFeの微粒子を噴霧したものを用いる方法は、収量も多くすることが可能で、工業的には好ましいが、金属Feの微粒子は反応性が高く、大気中で扱うことは出来ない。また、粉塵爆発の危険も無視できず、やはり対策が必要である。

【0009】一方、気相成長法には、COを熱分解する方法もあるが、COは爆発性のほかに、極めて強い毒性があり、許容濃度は50ppmと非常に厳しいものである。安全対策がコスト上昇要因になることは明白である。

【0010】したがった、工業的生産に適し、低温のプロセスで、安全対策が容易で、大気中で扱えるプロセスによって構成された気相成長炭素繊維の製造方法が求められている。

【0011】本発明は、これらの問題点を解決する新規の製造方法を検討した結果到達したものであり、炭化水

素ガスの熱分解によって炭素を気相成長することにより、工業的生産に適用可能で、高温のプロセスや、特別な安全対策など困難なプロセスを必要としない気相成長炭素繊維の製造方法を提供することを目的とするものである。

【0012】

【課題を解決するための手段】即ち、本発明は、耐熱性の基体上に触媒微粒子を分散してなる基板を不活性ガスで希釈した炭化水素ガスに曝露して熱処理し、炭化水素ガスの熱分解を行う工程を有することを特徴とする気相成長炭素繊維の製造方法である。

【0013】以下、本発明を詳細に説明する。本発明は、炭化水素ガスの熱分解によって気相成長炭素繊維を得る方法である。炭化水素ガスは可燃性であるが、不活性ガスで希釈することにより安全に取り扱うことが出来、特別な防爆設備を必要としない。また、毒性は、ガス種により異なるが、普通深刻な危険性はなく、希釈された状態では、酸欠防止のため十分な換気を行うことで十分である。

【0014】基板としては、耐熱性の基体上に触媒微粒子を分散してなる基板を用いる。触媒微粒子としては、金属Pd微粒子を分散配置したものが好ましい。Pd表面は、炭化水素の分解反応に顕著な触媒能を有し、低温での反応が可能である。また、後述するように、微粒子の形成工程は非常に容易に実現できる。

【0015】また、基板上に金属Pd微粒子を形成する方法は、絶縁性基体に有機Pd錯体溶液を塗布する工程と、該有機Pd錯体溶液を塗布した基体を大気中または酸化雰囲気中で熱処理しPdOとする工程と、該PdOを不活性ガスで希釈した還元性ガス中で熱処理して金属Pdとする工程を有する方法により行なうことができる。

【0016】絶縁性基体に塗布する有機Pd錯体溶液としては、例えば酢酸Pdのアミン錯体を酢酸ブチルに溶かした溶液が挙げられる。

【0017】前記PdOを不活性ガスで希釈した還元性ガスで熱処理する工程において、該還元性ガスとしては、 H_2 ガス、COガス、 C_2H_4 ガス等が挙げられるが、その中で H_2 ガスが好ましい。還元性ガスの濃度は、該ガス種の爆発範囲下限未満、 H_2 ガスの場合4vol%未満、特に1~3vol%が好ましい。

【0018】また、PdOを不活性ガスで希釈した還元性ガスで熱処理して金属Pdとする工程において、該還元性ガスとして炭化水素ガスを用いることができる。この炭化水素ガスは気相成長炭素繊維の製造方法に用いるものと同一の炭化水素ガスを用いると、PdOの金属Pdへの還元反応と炭素繊維の気相成長を同時に行うことができるので好ましい。

【0019】また本発明において、不活性ガスで希釈した炭化水素ガスを用いる還元及び熱分解の工程におい

て、炭化水素ガスとしては、例えば C_2H_4 、 C_3H_6 、 C_2H_6 、 CH_4 等が挙げられ、特に C_2H_4 が好ましい。また、不活性ガスで希釈した炭化水素ガスの濃度は、該ガス種の爆発範囲下限未満、 C_2H_4 ガスの場合通常は2.7vol%未満であり、好ましくは0.1~2vol%が望ましい。2.7vol%を越えると、防爆のための処置が必要で好ましくない。

【0020】不活性ガスとしては、特に制限することはないが、例えば窒素ガス、ヘリウムガス、アルゴンガスが用いられる。

【0021】また、炭化水素ガスの熱分解工程の熱処理温度は、450℃以上、好ましくは500~900℃が望ましい。450℃未満では、Pd微粒子表面での熱分解が生じなくなるので好ましくない。

【0022】

【実施例】以下実施例に基づき本発明を説明する。

【0023】実施例1

表面酸化膜を形成したシリコン基板を有機溶剤で洗浄した後、有機Pd錯体溶液をスピナーコートした。有機Pd錯体溶液は、奥野製薬(株)製：ccp4230を酢酸ブチルで5倍に希釈したものをを用いた。スピナーコートの条件は、800rpm、30秒である。

【0024】これを大気中で、300℃で12分間熱処理した。同じ条件で作製した試料をX線回折で調べたところ、酸化Pd(PdO)になっており、他の相は存在しなかった。

【0025】続いて、 N_2 (98vol%)+ H_2 (2vol%)の混合ガス気流中で、185℃、10分間の熱処理を行った。これを、走査電子顕微鏡で観察したところ、シリコン基板上にφ5nm程度の微粒子が分散していることが確かめられた。同じ条件で作製した試料のX線回折によると、金属Pdに変化しており、他の相は見られなかった。

【0026】続いて、Ar(99vol%)+ C_2H_4 (1vol%)の混合ガスと、 N_2 を1:9で混合した(したがって、 C_2H_4 :0.1vol%)気流中で、700℃、10分間の熱処理を行った。

【0027】これを走査電子顕微鏡で観察したところ、図1の走査電子顕微鏡写真(倍率×100,000)に示すように、φ10nm程度の繊維状のものが形成されていることがわかった。ラマン分光分析、およびX線光電子分光分析(XPS)の結果から、これが炭素であることが確認された。

【0028】目視では、基板上に黒色の粉体が堆積しているように見え、刷毛で軽く擦ると容易に剥離する。剥離した粉体を集め、透過電子顕微鏡で観察したところ、図2の透過電子顕微鏡写真(倍率×2,000,000)に示す様に、気相成長炭素繊維に特徴的な外周部の格子像が見られた。また、中心部には格子像が見えないことから内部は中空になっていると思われる。

【0029】実施例2

実施例1と同様に、表面酸化膜を有するシリコン基板上に有機Pd錯体溶液をスピンナーコートし、300℃の熱処理によりPdOを形成した後、25℃で60分間N₂（98vol%）+H₂（2vol%）混合ガス気流に曝露した。これを走査電子顕微鏡で観察したところ、形がやや不規則であるが、実施例1と同様に微粒子が形成されていることがわかった。X線回折により、金属Pdになっていることも確認された。

【0030】これを実施例1と同様に、C₂H₄：0.1vol%気流中で700℃、10分間の熱処理を行った。これを走査電子顕微鏡により観察したところ、実施例1と同様にφ10nm程度の気相成長炭素繊維が形成されていた。

【0031】実施例3

実施例1と同様に、表面酸化膜を形成したシリコン基板上に、Pd微粒子の分散膜を形成し、これをC₂H₄：0.1vol%気流中で450℃、10分間の熱処理を行った。これを走査電子顕微鏡で観察したところ、φ7nm程度のチューブが形成されていた。ラマン分光分析によりこれが炭素であることが確認された。

【0032】実施例4

実施例1と同様に、表面酸化膜を形成したシリコン基板上に、PdO膜を形成した後、N₂-H₂気流中で還元する工程を省いて、C₂H₄：0.1vol%気流中で700℃、10分間の熱処理を行った。これをラマン分光分析、走査電子顕微鏡観察により調べたところ、実施例1と同様の結果が得られた。

【0033】比較例1

実施例1と同様に、表面酸化膜を形成したシリコン基板上に、Pd微粒子の分散膜を形成し、これをC₂H₄：0.1vol%気流中で、400℃、10分間の熱処理を行った。これをラマン分光分析により調べたところ、炭素の信号は、通常大気中に放置した際に生ずる汚染によるもの程度の大きさで、熱分解による炭素は形成されていないことがわかった。

【0034】比較例2

石英基板を中性洗剤と有機溶剤により洗浄し、真空蒸着法により、厚さ300nmのPd薄膜を成膜した。これをC₂H₄：0.1vol%気流中で、700℃、10分間の熱処理を行った。ラマン分光分析の結果、炭素が堆積していることがわかった。しかし走査電子顕微鏡観察により、気相成長炭素繊維は形成されておらず、網目状に切れ目の入った炭素の膜が形成されていることが判明した。

【0035】実施例4については、本発明者らはここで用いたのと同じ雰囲気中で、PdOを熱処理することにより、180℃以上で還元され金属Pdとなることを確かめた。熱分解が起こるのは比較例1に示した様に400℃より高温であるから、熱分解が始まる前にPd微粒子が形成され実施例1と同様の結果が得られたものと思われる。

【0036】上記実施例においては、Pd微粒子形成方法として、有機錯体溶液塗布、酸化、還元という工程を用いたが、これに限定されるものではなく、ガス中蒸着法その他により微粒子形成を行った場合でも同様の効果が得られる。

【0037】基板は、シリコンに限定されることなく、耐熱性で、炭化水素の熱分解の触媒能が無い、小さい物質、たとえば石英基板など、ならば使用可能である。H₂およびC₂H₄の濃度は実施例に限定されるものではなく、爆発限界以下の濃度であれば、特別な防爆設備を必要としない。ちなみにH₂の爆発範囲下限は4vol%、C₂H₄は2.7vol%である。

【0038】熱分解工程における炭化水素ガスは、実施例に限定されるものではない。Pd金属表面における分解反応は、メタン、エタン、プロピレンなど多くのガス種で同様に起こることが知られており、当然本発明に適用可能である。また、エタノール、アセトンなど通常の状態では液体である炭化水素も、熱処理を減圧状態で行うなどして使用することが可能である。

【0039】また、本発明を用い、有機Pd錯体溶液をスクリーン印刷などの手法で適当なパターンに形成すれば、基板上の所望の位置にのみ気相成長炭素繊維を形成することが可能となる。これにより、気相成長炭素繊維を量子細線として用いる電子素子など新規な素子の製造が可能になる。

【0040】

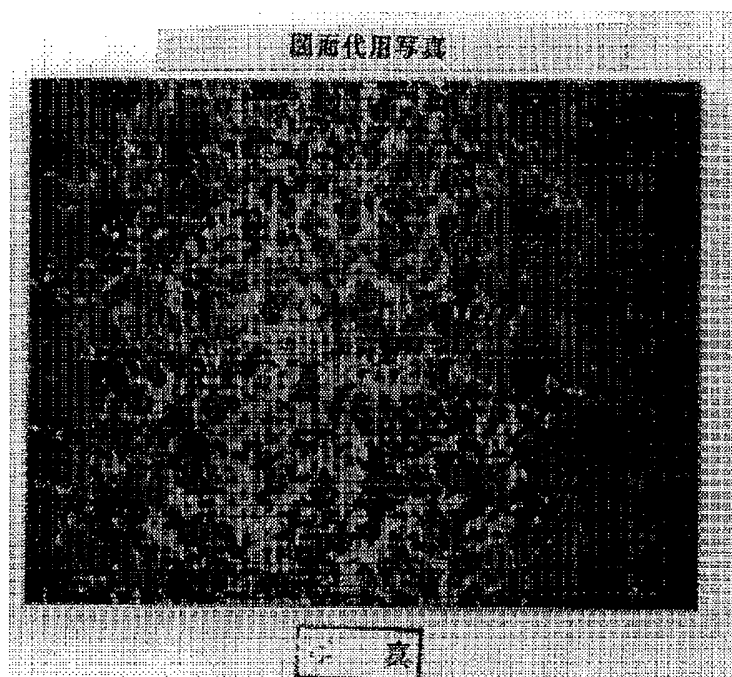
【発明の効果】以上説明した様に、本発明により、工業的生産に適用可能で、高温のプロセスや、特別な安全対策など困難なプロセスを必要としない気相成長炭素繊維の製造方法を実現することが可能となった。

【図面の簡単な説明】

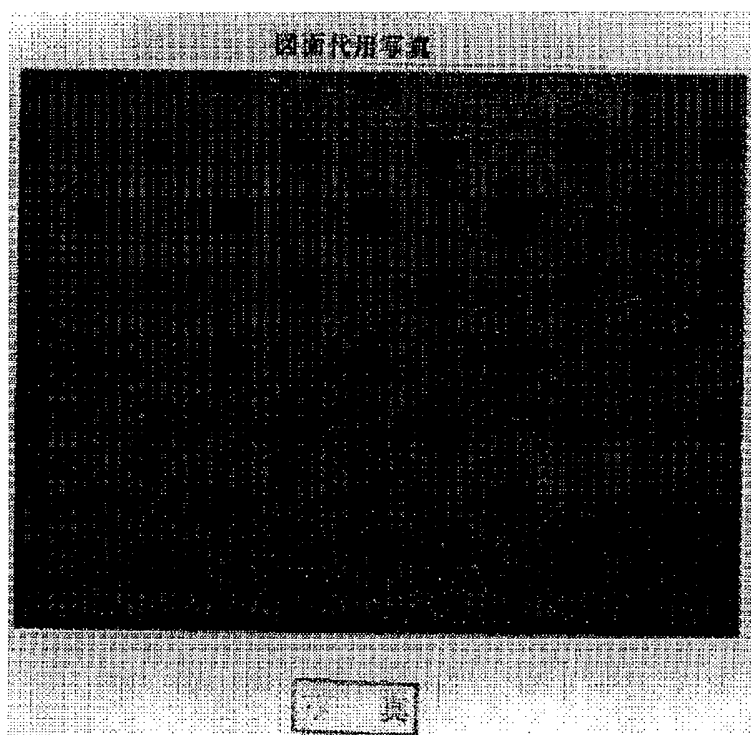
【図1】実施例1により、シリコン基板上に形成された気相成長炭素繊維の形状を示す走査電子顕微鏡写真（倍率×100,000）である。

【図2】実施例1により形成された気相成長炭素繊維の形状を示す透過電子顕微鏡写真（倍率×2,000,000）である。

【図1】



【図2】



PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-100328
(43)Date of publication of application : 16.04.1996

(51)Int.Cl. D01F 9/127
C01B 31/02

(21)Application number : 06-259030 (71)Applicant : CANON INC
(22)Date of filing : 29.09.1994 (72)Inventor : KISHI FUMIO
ISHIZAKI AKIYOSHI
TAKADA KAZUHIRO

(54) PRODUCTION OF CARBON FIBER BY VAPOR PHASE GROWTH

(57)Abstract:

PURPOSE: To obtain the subject carbon fiber without necessitating a high- temperature process and particular safety measures by thermally decomposing a hydrocarbon gas with a substrate having catalyst particles dispersed on a heat-resistant substrate.

CONSTITUTION: A substrate holding catalyst particles such as fine particles of metallic Pd dispersed on a heat-resistant substrate is exposed to a hydrocarbon gas (preferably C₂H₄) diluted with an inert gas and heat-treated to effect the thermal decomposition of the hydrocarbon gas and the vapor-phase growth of carbon fiber. An electronic element, etc., holding the vapor-phase grown carbon fiber as quantum fine line can be produced by forming a proper pattern of the catalyst particles by screen printing, etc.

LEGAL STATUS

[Date of request for examination] 27.06.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 3285284

[Date of registration] 08.03.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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[Claim(s)]

[Claim 1] The manufacture approach of the vapor growth carbon fiber characterized by having the process which exposes and heat-treats the substrate which comes to distribute a catalyst particle on a heat-resistant base in the hydrocarbon gas diluted with inert gas, and performs the pyrolysis of hydrocarbon gas.

[Claim 2] The manufacture approach of a vapor growth carbon fiber according to claim 1 that said catalyst particle is Metal Pd.

[Claim 3] The manufacture approach of a vapor-growth carbon fiber according to claim 2 of having the process at which the formation approach of the above-mentioned metal Pd particle applies organic Pd complex solution to an insulating base, the process which heat-treats the base with which this organic Pd complex solution was applied in atmospheric air or an oxidizing atmosphere, and sets to PdO, and the process which heat-treats in this reducibility gas by which PdO was diluted with inert gas, and uses as Metal Pd in the manufacture approach of said vapor-growth carbon fiber.

[Claim 4] It sets at the process which heat-treats said PdO by the reducibility gas diluted with inert gas, and this reducibility gas is H₂. The manufacture approach of the vapor growth carbon fiber according to claim 3 which is gas.

[Claim 5] H₂ which diluted said PdO with inert gas It sets at the process heat-treated by gas, and is H₂. The manufacture approach of a vapor growth carbon fiber according to claim 4 that concentration is less than [4vol%].

[Claim 6] It sets at the process heat-treated by the reducibility gas diluted with said inert gas according to claim 3, and is the manufacture approach of a vapor growth carbon fiber given in claim 1 as hydrocarbon gas according to claim 1 with this same reducibility gas thru/or one term of 3.

[Claim 7] the process of the reduction using the hydrocarbon gas diluted with said inert gas according to claim 1 or 6, and a pyrolysis -- setting -- this hydrocarbon gas -- C two H₄ it is -- the manufacture approach of a vapor growth carbon fiber according to claim 1 or 6.

[Claim 8] C two H₄ diluted with said inert gas The manufacture approach of a vapor growth carbon fiber according to claim 7 that concentration is less than [2.7vol%].

[Claim 9] The manufacture approach of a vapor growth carbon fiber according to claim 1 that the heat treatment temperature of the pyrolysis process of said hydrocarbon gas is 450 degrees C or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention offers the manufacture approach of the vapor growth carbon fiber which can be mass-produced on the manufacture approach of a vapor growth carbon fiber, especially industrial engineering, using a easier process.

[0002]

[Description of the Prior Art] Conventionally, it consists of 60 carbon atoms, the whole family of the fullerene which has been a carbonaceous cluster since the extensive synthesis method with football-like structure of C₆₀ was reported (Kratschmer, et.al.:Nature 347 (1990) 354), and various properties of a carbon nanotube with the structure which extended this to the one direction are interesting, and much researches are done.

[0003] It attracted attention that the superconductivity in which the crystal of C₆₀ which doped the alkali-metal atom especially has high critical temperature is shown. In addition, an electronic device with these new carbon clusters and the application as solid-state lubricant etc. are expected, and flourishing research is advanced aiming at the application from various viewpoints.

[0004] A vapor growth carbon fiber has good crystallinity as compared with the carbon fiber which carbonized hydrocarbon resin fiber at the elevated temperature although it was a little bigger cluster than a carbon nanotube, and the characteristic application is expected.

[0005] The typical method of manufacturing current and this vapor growth carbon fiber is the vapor growth by the pyrolysis of benzene. This approach is contacted with the steam of the benzene which used iron compounds, such as an iron oxide, as the substrate, and made the hydrogen of a high grade carrier gas at about 950-1000 degrees C. First, some substrates are returned and Fe particle is formed. By the catalyst ability on this front face of a particle, carbon begins to deposit on a front face. Growth is continued, while this carbon grows fibrous behind Fe particle and raises a particle.

[0006] By this approach, existence of Fe particle is indispensable and the approach using what sprayed the metal Fe particle on the substrate is also performed. (Michio Inagaki: "carbon material engineering" 72 pages, Nikkan Kogyo Shimbun issue 1985)

[0007]

[Problem(s) to be Solved by the Invention] Although the above-mentioned approach is industrially available, there are some troubles. An about 1000-degree C hot process is required for the 1st in process, equipment becomes large-scale, and there is a possibility that consumption of power may cause a cost rise, such as being large. In order to use [2nd] the hydrogen of a high grade, the cure of an explosion avoid accident is needed. Especially, a severe cure is demanded from especially using for the above-mentioned hot process, and there is a possibility that this may also cause a cost rise, from it.

[0008] Moreover, although the approach using what sprayed the particle of Fe on the substrate can be made [many] and is industrially desirable, the particle of Metal Fe has high reactivity and cannot be treated in atmospheric air. [of yield] Moreover, the risk of dust explosion cannot be disregarded, either but a cure is required too.

[0009] On the other hand, although there is also the approach of pyrolyzing CO in vapor growth, CO has very strong toxicity besides explosivity, threshold limit value is very as severe as 50 ppm, and it is clear that a safety practice causes a cost rise.

[0010] By being suitable for the industrial production which followed, in the low-temperature process, a safety practice is easy and the manufacture approach of the vapor growth carbon fiber constituted by the process which can be treated in atmospheric air is searched for.

[0011] By reaching, as a result of examining the new manufacture approach which solves these troubles, and carrying out vapor growth of the carbon by the pyrolysis of hydrocarbon gas, this invention can be applied to industrial production and aims at offering the manufacture approach of the vapor growth carbon fiber which needs neither a hot process nor a process with a special difficult safety practice etc.

[0012]

[Means for Solving the Problem] That is, this invention is the manufacture approach of the vapor growth carbon fiber characterized by having the process which exposes and heat-treats the substrate which comes to distribute a catalyst particle on a heat-resistant base in the hydrocarbon gas diluted with inert gas, and performs the pyrolysis of hydrocarbon gas.

[0013] Hereafter, this invention is explained to a detail. This invention is the approach of obtaining a vapor growth carbon fiber by the pyrolysis of hydrocarbon gas. Although hydrocarbon gas is inflammability, by diluting with inert gas, it can be dealt with safely and does not need a special explosion-proof facility. Moreover, although toxicity changes with types of gas, there is no usually serious danger and it is enough as it to perform sufficient ventilation in the condition of having diluted, for oxygen-deficiency prevention.

[0014] As a substrate, the substrate which comes to distribute a catalyst particle is used on a heat-resistant base. As a catalyst particle, what distributed the metal Pd particle is desirable. Pd front face has catalyst ability remarkable in the decomposition reaction of a hydrocarbon, and the reaction in low temperature is possible for it. Moreover, the formation process of a particle can be realized very easily so that it may mention later.

[0015] Moreover, the approach of forming a metal Pd particle on a substrate can be performed by the approach of having the process which applies organic Pd complex solution to an insulating base, the process which heat-treats the base which applied this organic Pd complex solution in atmospheric air or an oxidizing atmosphere, and is set to PdO, and the process which heat-treats in this reducibility gas that diluted PdO with inert gas, and is used as Metal Pd.

[0016] As an organic Pd complex solution applied to an insulating base, the solution which melted the amine complex of an acetic acid Pd to butyl acetate, for example is mentioned.

[0017] It sets at the process which heat-treats said PdO by the reducibility gas diluted with inert gas, and is H₂ as this reducibility gas. Although gas, CO gas, C₂H₄ gas, etc. are mentioned, it is H₂ in it. Gas is desirable. the concentration of reducibility gas -- the case of under the range-of-explosion minimum of this type of gas, and H₂ gas -- less than [4vol%] -- 1 - 3vol% is especially desirable.

[0018] Moreover, in the process which heat-treats by the reducibility gas which diluted PdO with inert gas, and is used as Metal Pd, hydrocarbon gas can be used as this reducibility gas. If the same hydrocarbon gas as what is used for the manufacture approach of a vapor growth carbon fiber is used, since this hydrocarbon gas can perform reduction reaction to the metal Pd of PdO, and vapor growth of a carbon fiber to coincidence, it is desirable.

[0019] Moreover, in the process of the reduction using the hydrocarbon gas diluted with inert gas in this invention, and a pyrolysis, C two H₄, C₃H₆, C₂H₆, and CH₄ grade are mentioned as hydrocarbon gas, for example, and it is especially C two H₄. It is desirable. Moreover, in the case of C₂H₄ gas, the concentration of the hydrocarbon gas diluted with inert gas is usually less than [2.7vol%], and is preferably [0.1 - 2vol% of] desirable under the range-of-explosion minimum of this type of gas. 2. If 7vol% is exceeded, the treatment for explosion protection is required and is not desirable.

[0020] especially as inert gas, nitrogen gas, gaseous helium, and argon gas are used for restricting 7 **.

[0021] Moreover, the heat treatment temperature of the pyrolysis process of hydrocarbon gas has preferably desirable 500-900 degrees C 450 degrees C or more. Since the pyrolysis in Pd particle front face stops arising at less than 450 degrees C, it is not desirable.

[0022]

[Example] Based on an example, this invention is explained below.

[0023] After the organic solvent washed the silicon substrate in which the example 1 scaling film was formed, the spinner coat of the organic Pd complex solution was carried out. organic Pd complex solution -- the product made from Okuno Pharmaceuticals -- what diluted :ccp4230 with butyl acetate 5 times was used. The conditions of a spinner coat are 800rpm and 30 seconds.

[0024] This was heat-treated for 12 minutes at 300 degrees C in atmospheric air. When the sample produced on the same conditions was investigated by the X diffraction, it is Oxidation Pd (PdO) and other phases did not exist.

[0025] Then, 185 degrees C and heat treatment for 10 minutes were performed in the mixed-gas air current of N₂+ (98vol%) H₂ (2vol%). When this was observed with the scanning electron microscope, it was confirmed that the about [phi5nm] particle is distributing on a silicon substrate. According to the X diffraction of the sample produced on the same conditions, it was changing to Metal Pd and other phases were not seen.

[0026] Then, 700 degrees C and heat treatment for 10 minutes were performed in the air current (C₂ H₄ : therefore, 0.1vol%) which mixed N₂ with the mixed gas of Ar(99vol%)+C two H₄ (1vol%) by 1:9.

[0027] When this was observed with the scanning electron microscope, as shown in the scanning electron microscope photograph (scale-factor x100,000) of drawing 1 , it turned out that the about [phi10nm] fibrous thing is formed. It was checked from the result of Raman spectroscopic analysis and X-ray-photoelectron-spectroscopy analysis (XPS) that this is carbon.

[0028] Visually, if it seems that black fine particles have deposited and grinds lightly with the brush on a substrate, it will exfoliate easily. When the fine particles which exfoliated were collected and having been observed with the transmission electron microscope, as shown in the transmission electron microscope photograph (scale-factor x2,000,000) of drawing 2, the lattice image of the periphery section characteristic of a vapor growth carbon fiber was seen. Moreover, since a lattice image is not visible to a core, it is thought that the interior has become in midair.

[0029] After carrying out the spinner coat of the organic Pd complex solution to the silicon substrate which has the scaling film like example 2 example 1 and forming PdO by 300-degree C heat treatment, it was exposed to the N₂+ (98vol%) H₂ mixed-gas (2vol%) air current for 60 minutes at 25 degrees C. Although the form was a little irregular when this was observed with the scanning electron microscope, it turned out that the particle is formed like an example 1. It was also checked according to the X diffraction that it is Metal Pd.

[0030] this -- an example 1 -- the same -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. When this was observed with the scanning electron microscope, the about [phi10nm] vapor growth carbon fiber was formed like the example 1.

[0031] the silicon substrate top which formed the scaling film like example 3 example 1 -- the distributed film of Pd particle -- forming -- this -- C two H₄ : 0.1vol% -- 450 degrees C and heat treatment for 10 minutes were performed in the air current. When this was observed with the scanning electron microscope, the about [phi7nm] tube was formed. It was checked by Raman spectroscopic analysis that this is carbon.

[0032] N₂-H₂ after forming the PdO film on the silicon substrate in which the scaling film was formed, like example 4 example 1 the process returned in an air current -- excluding -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. When Raman spectroscopic analysis and scanning electron microscope observation investigated this, the same result as an example 1 was obtained.

[0033] the silicon substrate top which formed the scaling film like example of comparison 1 example 1 -- the distributed film of Pd particle -- forming -- this -- C two H₄ : 0.1vol% -- 400 degrees C and heat treatment for 10 minutes were performed in the air current. When Raman spectroscopic analysis investigated this, a carbonaceous signal is the magnitude of thing extent depended on the contamination produced when it is usually left in atmospheric air, and it turned out that the carbon by the pyrolysis is not formed.

[0034] Neutral detergent and an organic solvent washed the example of comparison 2 quartz substrate, and Pd thin film with a thickness of 300nm was formed with the vacuum deposition method. this -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. Raman spectroscopic analysis showed that carbon had accumulated. However, it became clear that a vapor growth carbon fiber was not formed of scanning electron microscope observation, but the film of the carbon into which the break went in the shape of a mesh was formed.

[0035] About the example 4, this invention persons confirmed it being returned above 180 degrees C and becoming Metal Pd by heat-treating PdO, in the same ambient atmosphere as having used here. It is considered with like that Pd particle was formed and the same result as an example 1 was obtained from 400 degrees C before [which was shown in the example 1 of a comparison] the pyrolysis started since it was an elevated temperature that a pyrolysis happens.

[0036] In the above-mentioned example, although the process of organic complex solution spreading, oxidation, and reduction was used as the Pd particle formation approach, it is not limited to this, and even when the vacuum deposition in gas and others perform particle formation, the same effectiveness is acquired.

[0037] Without being limited to silicon, it is thermal resistance, a substrate does not have the catalyst ability of the pyrolysis of a hydrocarbon, or the small matter, for example, a quartz substrate etc., is usable [the substrate], if it becomes. H₂ And C two H₄ Concentration is not limited to an example, and if it is the concentration below the explosion limit, it does not need a special explosion-proof facility. Incidentally it is H₂. A range-of-explosion minimum is 4vol(s)% and C two H₄. It is 2.7vol(s)%.

[0038] The hydrocarbon gas in a pyrolysis process is not limited to an example. Happening similarly is known for many types of gas, such as methane, ethane, and a propylene, and, naturally the decomposition reaction in Pd surface of metal can be applied to this invention. Moreover, it is possible for hydrocarbons which are liquids in the usual condition, such as ethanol and an acetone, to also heat-treat, and to use them in the state of reduced pressure.

[0039] Moreover, if organic Pd complex solution is formed in a suitable pattern by technique, such as screen-stencil, using this invention, it will become possible to form a vapor growth carbon fiber only in the location of the request on a substrate. Thereby, manufacture of new components, such as an electronic device using a vapor growth carbon fiber as quantum wire, is attained.

[0040]

[Effect of the Invention] It became possible to realize the manufacture approach of the vapor growth carbon fiber which can apply to industrial production by this invention like, and needs neither a hot process nor a process with a special difficult safety practice etc. explained above.

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PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-100328

(43)Date of publication of application : 16.04.1996

(51)Int.Cl.

D01F 9/127
C01B 31/02

(21)Application number : 06-259030

(71)Applicant : CANON INC

(22)Date of filing : 29.09.1994

(72)Inventor : KISHI FUMIO

ISHIZAKI AKIYOSHI

TAKADA KAZUHIRO

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(57)Abstract:

PURPOSE: To obtain the subject carbon fiber without necessitating a high- temperature process and particular safety measures by thermally decomposing a hydrocarbon gas with a substrate having catalyst particles dispersed on a heat-resistant substrate.

CONSTITUTION: A substrate holding catalyst particles such as fine particles of metallic Pd dispersed on a heat-resistant substrate is exposed to a hydrocarbon gas (preferably C₂H₄) diluted with an inert gas and heat-treated to effect the thermal decomposition of the hydrocarbon gas and the vapor-phase growth of carbon fiber. An electronic element, etc., holding the vapor-phase grown carbon fiber as quantum fine line can be produced by forming a proper pattern of the catalyst particles by screen printing, etc.

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[0008] Moreover, although the approach using what sprayed the particle of Fe on the substrate can be made [many] and is industrially desirable, the particle of Metal Fe has high reactivity and cannot be treated in atmospheric air. [of yield] Moreover, the risk of dust explosion cannot be disregarded, either but a cure is required too.

[0009] On the other hand, although there is also the approach of pyrolyzing CO in vapor growth, CO has very strong toxicity besides explosivity, threshold limit value is very as severe as 50 ppm, and it is clear that a safety practice causes a cost rise.

[0010] By being suitable for the industrial production which followed, in the low-temperature process, a safety practice is easy and the manufacture approach of the vapor growth carbon fiber constituted by the process which can be treated in atmospheric air is searched for.

[0011] By reaching, as a result of examining the new manufacture approach which solves these troubles, and carrying out vapor growth of the carbon by the pyrolysis of hydrocarbon gas, this invention can be applied to industrial production and aims at offering the manufacture approach of the vapor growth carbon fiber which needs neither a hot process nor a process with a special difficult safety practice etc.

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[Means for Solving the Problem] That is, this invention is the manufacture approach of the vapor growth carbon fiber characterized by having the process which exposes and heat-treats the substrate which comes to distribute a catalyst particle on a heat-resistant base in the hydrocarbon gas diluted with inert gas, and performs the pyrolysis of hydrocarbon gas.

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[0017] It sets at the process which heat-treats said PdO by the reducibility gas diluted with inert gas, and is H₂ as this reducibility gas. Although gas, CO gas, C₂H₄ gas, etc. are mentioned, it is H₂ in it. Gas is desirable. the concentration of reducibility gas -- the case of under the range-of-explosion minimum of this type of gas, and H₂ gas -- less than [4vol%] -- 1 - 3vol% is especially desirable.

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[0020] especially as inert gas, nitrogen gas, gaseous helium, and argon gas are used for restricting 7 **.

[0021] Moreover, the heat treatment temperature of the pyrolysis process of hydrocarbon gas has preferably desirable 500-900 degrees C 450 degrees C or more. Since the pyrolysis in Pd particle front face stops arising at less than 450 degrees C, it is not desirable.

[0022]

[Example] Based on an example, this invention is explained below.

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[0024] This was heat-treated for 12 minutes at 300 degrees C in atmospheric air. When the sample produced on the same conditions was investigated by the X diffraction, it is Oxidation Pd (PdO) and other phases did not exist.

[0025] Then, 185 degrees C and heat treatment for 10 minutes were performed in the mixed-gas air current of N₂+ (98vol%) H₂ (2vol%). When this was observed with the scanning electron microscope, it was confirmed that the about [phi5nm] particle is distributing on a silicon substrate. According to the X diffraction of the sample produced on the same conditions, it was changing to Metal Pd and other phases were not seen.

[0026] Then, 700 degrees C and heat treatment for 10 minutes were performed in the air current (C₂ H₄ : therefore, 0.1vol%) which mixed N₂ with the mixed gas of Ar(99vol%)+C two H₄ (1vol%) by 1:9.

[0027] When this was observed with the scanning electron microscope, as shown in the scanning electron microscope photograph (scale-factor x100,000) of drawing 1 , it turned out that the about [phi10nm] fibrous thing is formed. It was checked from the result of Raman spectroscopic analysis and X-ray-photoelectron-spectroscopy analysis (XPS) that this is carbon.

[0028] Visually, if it seems that black fine particles have deposited and grinds lightly with the brush on a substrate, it will exfoliate easily. When the fine particles which exfoliated were collected and having been observed with the transmission electron microscope, as shown in the transmission electron microscope photograph (scale-factor x2,000,000) of drawing 2, the lattice image of the periphery section characteristic of a vapor growth carbon fiber was seen. Moreover, since a lattice image is not visible to a core, it is thought that the interior has become in midair.

[0029] After carrying out the spinner coat of the organic Pd complex solution to the silicon substrate which has the scaling film like example 2 example 1 and forming PdO by 300-degree C heat treatment, it was exposed to the N₂+ (98vol%) H₂ mixed-gas (2vol%) air current for 60 minutes at 25 degrees C. Although the form was a little irregular when this was observed with the scanning electron microscope, it turned out that the particle is formed like an example 1. It was also checked according to the X diffraction that it is Metal Pd.

[0030] this -- an example 1 -- the same -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. When this was observed with the scanning electron microscope, the about [phi10nm] vapor growth carbon fiber was formed like the example 1.

[0031] the silicon substrate top which formed the scaling film like example 3 example 1 -- the distributed film of Pd particle -- forming -- this -- C two H₄ : 0.1vol% -- 450 degrees C and heat treatment for 10 minutes were performed in the air current. When this was observed with the scanning electron microscope, the about [phi7nm] tube was formed. It was checked by Raman spectroscopic analysis that this is carbon.

[0032] N₂-H₂ after forming the PdO film on the silicon substrate in which the scaling film was formed, like example 4 example 1 the process returned in an air current -- excluding -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. When Raman spectroscopic analysis and scanning electron microscope observation investigated this, the same result as an example 1 was obtained.

[0033] the silicon substrate top which formed the scaling film like example of comparison 1 example 1 -- the distributed film of Pd particle -- forming -- this -- C two H₄ : 0.1vol% -- 400 degrees C and heat treatment for 10 minutes were performed in the air current. When Raman spectroscopic analysis investigated this, a carbonaceous signal is the magnitude of thing extent depended on the contamination produced when it is usually left in atmospheric air, and it turned out that the carbon by the pyrolysis is not formed.

[0034] Neutral detergent and an organic solvent washed the example of comparison 2 quartz substrate, and Pd thin film with a thickness of 300nm was formed with the vacuum deposition method. this -- C two H₄ : 0.1vol% -- 700 degrees C and heat treatment for 10 minutes were performed in the air current. Raman spectroscopic analysis showed that carbon had accumulated. However, it became clear that a vapor growth carbon fiber was not formed of scanning electron microscope observation, but the film of the carbon into which the break went in the shape of a mesh was formed.

[0035] About the example 4, this invention persons confirmed it being returned above 180 degrees C and becoming Metal Pd by heat-treating PdO, in the same ambient atmosphere as having used here. It is considered with like that Pd particle was formed and the same result as an example 1 was obtained from 400 degrees C before [which was shown in the example 1 of a comparison] the pyrolysis started since it was an elevated temperature that a pyrolysis happens.

[0036] In the above-mentioned example, although the process of organic complex solution spreading, oxidation, and reduction was used as the Pd particle formation approach, it is not limited to this, and even when the vacuum deposition in gas and others perform particle formation, the same effectiveness is acquired.

[0037] Without being limited to silicon, it is thermal resistance, a substrate does not have the catalyst ability of the pyrolysis of a hydrocarbon, or the small matter, for example, a quartz substrate etc., is usable [the substrate], if it becomes. H₂ And C two H₄ Concentration is not limited to an example, and if it is the concentration below the explosion limit, it does not need a special explosion-proof facility. Incidentally it is H₂. A range-of-explosion minimum is 4vol(s)% and C two H₄. It is 2.7vol(s)%.

[0038] The hydrocarbon gas in a pyrolysis process is not limited to an example. Happening similarly is known for many types of gas, such as methane, ethane, and a propylene, and, naturally the decomposition reaction in Pd surface of metal can be applied to this invention. Moreover, it is possible for hydrocarbons which are liquids in the usual condition, such as ethanol and an acetone, to also heat-treat, and to use them in the state of reduced pressure.

[0039] Moreover, if organic Pd complex solution is formed in a suitable pattern by technique, such as screen-stencil, using this invention, it will become possible to form a vapor growth carbon fiber only in the location of the request on a substrate. Thereby, manufacture of new components, such as an electronic device using a vapor growth carbon fiber as quantum wire, is attained.

[0040]

[Effect of the Invention] It became possible to realize the manufacture approach of the vapor growth carbon fiber which can apply to industrial production by this invention like, and needs neither a hot process nor a process with a special difficult safety practice etc. explained above.

[Translation done.]